

Preparation and characterization of calcium cobaltite for thermoelectric application

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Abstract

Starting powders of CaCO_3 with different Ca:Co ratio and three different sources of cobalt (II,III) oxide were mixed and calcined at 700-1100°C. DTA/TG, mass changes, density, grain size distribution, phase composition were examined. It has been found that phase composition of the resulted product was dependent on calcination temperature and properties of starting cobalt oxide. Three stages of cobaltite formation were established: simultaneous decomposition of CaCO_3 with $\text{Ca}_3\text{Co}_4\text{O}_9$ formation (800-900 °C), decomposition of $\text{Ca}_3\text{Co}_4\text{O}_9$ and formation of $\text{Ca}_3\text{Co}_2\text{O}_6$ (about 950 °C) and the last stage at 1050°C was dependent on starting cation ratio and source of cobalt (II,III) oxide. It has been found that total decomposition of the previous phases was observed after calcinations at 1050 °C in the batches with Ca:Co=1:1 ratio if very pure Co_3O_4 was used for preparation. Replacement of pure Co_3O_4 by cobalt oxide contaminated by cobalt hydroxide lead to re-formation of $\text{Ca}_3\text{Co}_4\text{O}_9$ phase at 1050 °C in 1:1 batches. Residual Co_3O_4 and CaO was always present in calcined specimens. It seems that prolonged heat treatment did not lead to better reaction degree.

1. Introduction

The layered cobaltites as $\text{Ca}_3\text{Co}_4\text{O}_9$ (denoted as $[\text{Ca}_2\text{CoO}_3]_{0.62}\text{CoO}_2$] or Ca349) [1-2] and as $[\text{Ca}_2\text{Co}_2\text{O}_4]_{0.624}\text{CoO}_2$] (denoted as CCCO) [3] and as (Bi, Ca) Co_4O_9 [4] were lately reported as promising thermoelectric materials. They exhibit surprising thermoelectric properties due to a large thermopower S at room temperature with simultaneously small resistivity ρ . Their small thermal conductivity κ and good thermal stability up to 700 °C makes them a good example of the “electron crystal and phonon glass” [5], an ideal material for thermoelectric application. However, thermoelectric performance of that ceramic is lower than that of single crystals and little is known about processing and its parameters. They could influence the final microstructure and thermoelectric properties of the polycrystalline product. The aim of this paper is to study influence of temperature and source of cobalt oxide on calcium cobaltite formation.

2. Experimental procedure

Three different commercially available cobalt (II,III) oxide sources were tested: (1) reagent grade (POCH), (2) standard oxide (Przedsiębiorstwo Odczynniki Chemiczne Lublin) and (3) extra pure (ChemPur). A small amount of Co_3O_4 was prepared in laboratory by sol-gel method: cobalt acetate was added to solution of 10 mol citric acid and 5 mol ethyleneglicol, boiled and calcined at 500 °C. Properties of the oxides are shown in Table 1. Density of the powders was determined by helium pycnometer. Oxygen content was examined by TG study in hydrogen. Decomposition of the cobalt oxides was tested by DTA/TG study in air during heating and cooling. Co^{2+} content was determined after reaction with Franky’s reagent. Infrared spectroscopy was applied to all the oxides. Total cobalt content was examined by spectrophotometric determination of cobalt thiocyanate complexes and spectrophotometric analysis of cobalt complexes with DTA.

Calcium cobaltites were prepared by solid state reaction of CaCO_3 (POCH, Poland) and two different commercially available Co_3O_4 sources: pure (1) and standard (2). Two composition with Ca:Co cation ratio of 1:1 and 3:4 were chosen for synthesis. The stoichiometric amount of CaCO_3 and Co_3O_4 were mixed with Si_3N_4 balls in isopropyl alcohol for 24 hours. After drying the powder was uni-axially pressed (tablets with 10 mm diameter and 5-6 mm height)

and calcined in the open horizontal tube furnace at temperature range 800-1050 °C for 20 hrs. 3 tablets were placed in an alumina boat, each tablet was weighed out before and after calcinations. XRD study was performed on the powdered specimens. Other tablets were aged at room temperature and weighed after 10 and 20 days after calcinations.

DTA/TG study were applied to all the batches in flowing air at temperature range 20-1350 °C (NETZSCH STA 409). The relevant curves were recorded during heating and cooling down. Some specimens were observed in scanning electron microscope and EDS was done.

3. Results and discussion

Analysis of cobalt (II,III) oxide powder properties shows small differences of physical properties and thermal behavior (Table 1). Metal contaminants in all the examined powders are below 0.01 wt% level and can not change such properties as density or oxygen content. It is supposed that observed differences resulted from various cobalt oxidation state and relevant oxygen content. Oxide (2) contains small amount of cobalt hydroxide or hydrate, as confirmed by DTG and IR-study. However, the reason of lower decomposition temperature is not clear: presence of OH group or cations (Na, K, Al). Surface area of the tested powders does not affect decomposition of Co_3O_4 (thermally activated process) but does influence re-oxidation of CoO during cooling (heterogeneous reaction). Fig.1 shows mass gain of three oxides during cooling and it can be noticed that mass gain of oxide (2) with remarkable higher grain size is the lowest among the other oxides.

Summary results of DTA/TG study of 1:1 and 3:4 composition are shown in Table 2. Four endothermic reactions are found for each composition but only three first reactions are of interest. It could be seen that the first reaction of calcium carbonate decomposition and calcium cobaltite formation is the most influenced by cobalt oxide source and starting cation ratio. Cobalt oxide (2) exhibits lower temperature of the new compound formation in comparison to the pure oxide (1). Creation of the compound happens simultaneously with CaCO_3 decomposition in the 3:4 batches. In the case of 1:1 batches the relevant peak is splitted (oxide No 2) or separated into the two peaks (oxide No1). The one at higher temperature corresponds to decomposition of Co_3O_4 . Thus 3:4 cation ratio is the proper composition for the synthesis of low temperature cobaltite ($\text{Ca}_3\text{Co}_2\text{O}_9$).

Reactions at higher temperature cause further mass losses, they are reversible and are influenced by the powder surface area. Thus the second reaction involves decrease of average cobalt oxidation state and its re-oxidation during cooling. Exothermic peak during cooling at the same temperature as Co_3O_4 decomposition is accompanied by mass gain and could be treated as indication of the presence and amount of the non-reacted oxide. It must be stressed that $\text{CoO} \rightarrow \text{Co}_3\text{O}_4$ oxidation occurred in the all examined batches.

Isothermal calcinations results (Table 3, Fig.2) show that $\text{Ca}_3\text{Co}_2\text{O}_9$ phase was formed as a main phase at 850 °C (oxide 1) or at 800 °C (oxide 2). That temperature is much lower than reported calcinations/sintering temperature for that phase: 920 °C [1] or 1100 °C [4]. Calcination at higher temperature led to increase of $\text{Ca}_3\text{Co}_2\text{O}_9$ phase. Total or significant decomposition of $\text{Ca}_3\text{Co}_2\text{O}_9$ was observed after calcinations at 950 °C. Low-temperature formation of $\text{Ca}_3\text{Co}_2\text{O}_9$ at 800 °C was not completed after 20 hrs calcinations and traces of residual reagents (CaCO_3 and Co_3O_4) were detected by XRD. Increase of calcinations temperature up to 850 °C caused formation of a small amount of $\text{Ca}_3\text{Co}_2\text{O}_9$ and no traces of CaCO_3 were detected by XRD. On the other hand, presence of Co_3O_4 was detected by DTA/TG, if performed on the specimens after calcinations. Study of two various cation ratio composition shows that at the same temperature $\text{Ca}_3\text{Co}_2\text{O}_9$ phase forms more easily than $\text{Ca}_3\text{Co}_2\text{O}_9$ if 1:1 ratio is predominant in the tablets. It is supposed that local inhomogeneity inside 3:4 tablets could lead rather to formation of $\text{Ca}_3\text{Co}_2\text{O}_9$ phase than to the full completion of $\text{Ca}_3\text{Co}_2\text{O}_9$. Mass loss after isothermal calcinations (Fig.2) confirms various behavior of the batches prepared with different cation ratio and various Co_3O_4 sources. Higher mass losses for batches

composed from oxide (2) indicates higher reaction degree in specimens calcined up to 950 °C. Indeed, stoichiometric mass loss in the case of 1:1 tablets was achieved after 20 hrs calcination at 800 °C for oxide (2) in comparison to 900 °C for composition with oxide (1). Calcination above 950 °C shows two different reaction paths, if composition of the two various cobalt oxide source are compared. Isothermal annealing of tablets from oxide (1) above 950 °C led to increasing mass loss (oxygen depletion), while oxide (2) derived product exhibits lower mass loss. XRD study of product calcined at 1050 °C showed surprising results: re-formation of Ca₃Co₄O₉ phase in tablets from oxide (2) or cobaltite decomposition to starting oxides in tablets from oxide (1).

Summary

Source of cobalt (II,III) oxide could have decisive influence on the final phase composition of the calcinations product. Presence of residual OH group in starting cobalt oxide could decrease temperature of the relevant cobaltite formation. Ca₃Co₄O₉ phase with claimed thermoelectric properties could and should be obtained at such a low temperature as 800 or 850 °C. Presence of residual starting oxides after calcinations could be diminished by homogeneity improving rather than by higher temperature or prolonged calcinations.

References

1. Miyazaki Y., Kudo K., Akoshima M., Ono Y., Koike Y., Kajitani T. Low-temperature thermoelectric properties of the composite crystal [Ca₂CoO_{3.34}]_{0.614}[CoO₂]. *Jpn. J. Appl. Phys.* 2000, **39**, L531-L533
2. Horii S., Matsubara I., Fujie K., Shin W., Murayama N., Shimoyama J., Kishio K. Thermoelectric properties of grain-aligned Ca-based cobaltites by a magneto-scientific method. *Proc. 22 Int. Conf. on Thermoelectrics*, 2003, 239-242
3. Itahara H., Xia C., Seno Y., Sugiyama J., Tani T., Koumoto K. Synthesis of textured thermoelectric layered cobaltites by reactive templated grain growth. *Ibid* 188-191
4. Li S., Funahashi R., Matsubara I., Ueno K., Sodeoka S., Yamada H. Synthesis and thermoelectric properties of the new oxide materials Ca_{3-x}Bi_xCo₄O_{9+δ} (0.0<x<0.75) *Chem. Mater.* 2000, **12**, 2424-2427
5. Hebert S., Flahaut D., Pelloquin D., Martin C., Maignan A., Hejtmanek J. Cobalt oxides as potential thermoelectric elements: the influence of the dimensionality. *Proc. 22 Int. Conf. on Thermoelectrics*, 2003, 161-163

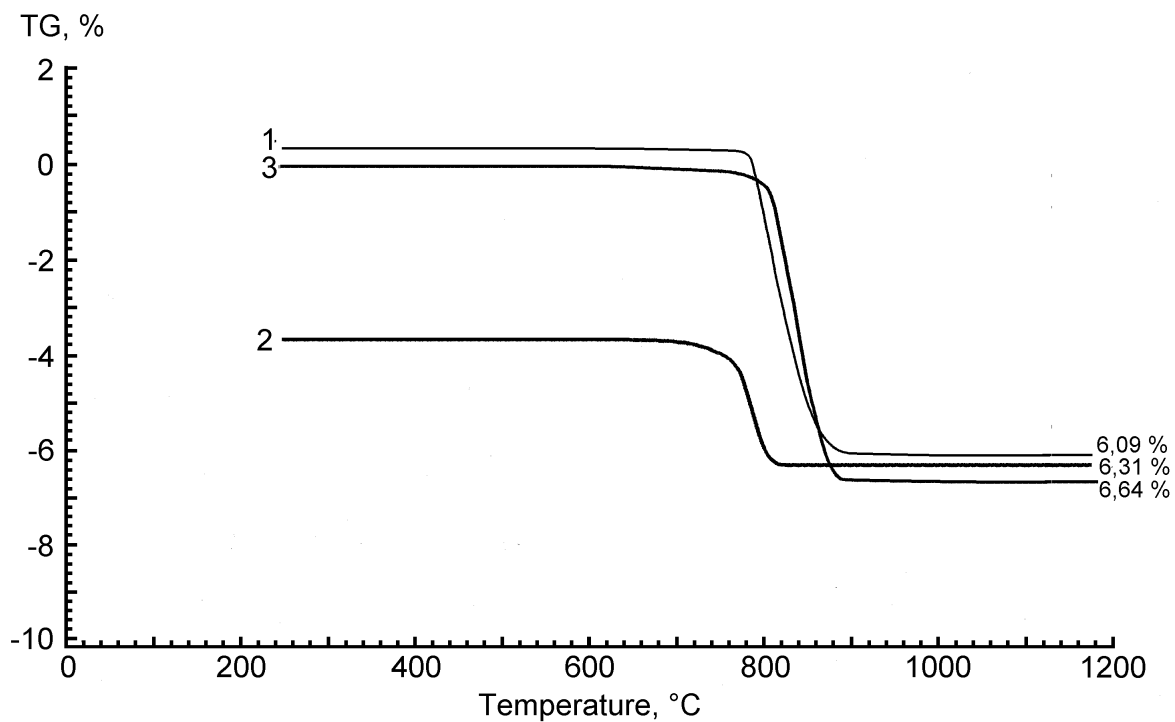


Fig.1 TG of cobalt oxides during cooling. Numbers on the left side refers to the number of the relevant oxide. Figures on the right side indicates mass loss as a result of heating up to 1200 °C.

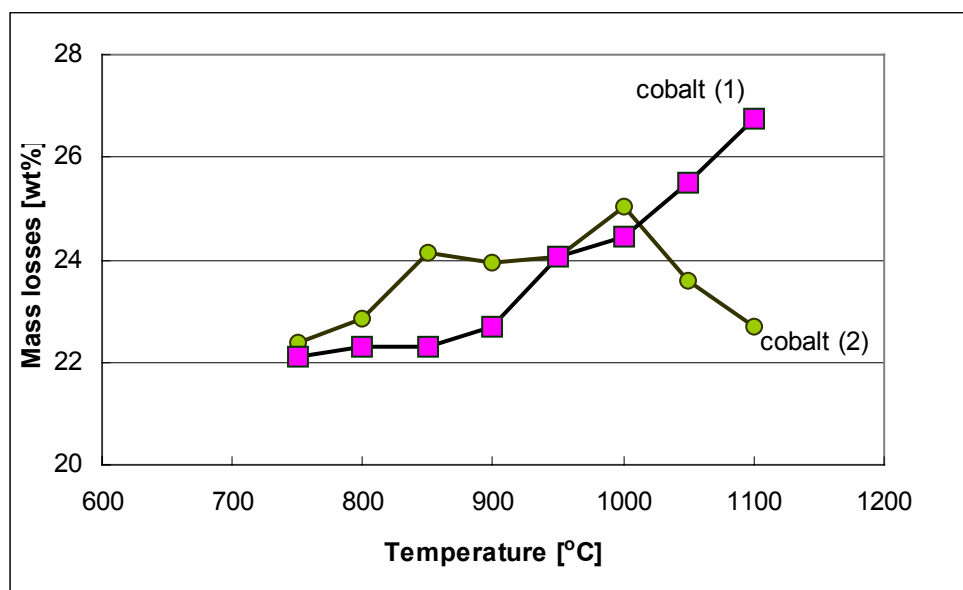


Fig.2 Mass losses of 1:1 composition after calcinations for 20 hrs vs temperature

Table 1 Properties of cobalt (II,III) oxides

	Total cobalt content [wt %]	Oxygen content [wt %]	Co ²⁺ content [wt %]	Temperature of decomposition [°C]	Oxygen loss of Co ₃ O ₄ decomposition)* [wt %]	Mass loss below decomposition [wt %]	Density [g/cm ³]	Average grain size d ₅₀ [μm]
(1) POCH	71.71	26.02	0.3	916	6.09	0.37	6.132	0.92
(2) Lublin	69.96	26.27	1.7	876	6.31	2.27)**	5.876	19.78
(3) ChemPur	72.6	26.39	0.1	916	6.64	0.0	6.114	4.36
(4) sol-gel				911	6.11	0.75		-
Stoichiometric	73.42	26.58	0.0	about 900	6.64	0.0	6.110	-

According to suppliers total metal contaminants (Na, K, Al, Ca) < 0.01 % in all the oxides

)* - according to reaction: $\text{Co}_3\text{O}_4 = 3\text{CoO} + \frac{1}{2} \text{O}_2$

)** - decomposition at 116 °C

Table 2 DTA/TG results of 1:1 and 3:4 batches prepared from pure (1) and standard (2)

cobalt(II,III) oxide

	Cation ratio	1 st reaction		2 nd reaction		3 rd reaction	
		Temp. _{max} [°C]	Mass loss [wt %]	Temp. _{max} [°C]	Mass loss [wt %]	Temp. _{max} [°C]	Mass loss [wt %]
Pure (1)	1 : 1	874 920	22.6	960	1.2	1059	2.4
Standard (2)	3 : 4	819	18.5	955	3.1	1039	2.3
	1 : 1	818 848	22.4	948	2.5	1041	2.4

Table 3

Phase composition of the tablets of 1:1 and 3:4 composition after calcinations for 20 hrs at given temperature

	Cation ratio	800 °C	850 °C	900 °C	950 °C	1050 °C
Pure (1)	1 : 1		Ca349 xxx Ca326 x	Ca 349 xx Ca326 xx	Ca349 - Ca326 xxxxx Ca(OH) ₂ x	Ca349 - Ca326 xx Co ₃ O ₄ x Ca(OH) ₂ xx
Standard (2)	1 : 1	Ca349 xxxxx CoO tr. Co ₃ O ₄ tr. CaCO ₃ tr.	Ca349 x Ca326 xxx	-	Ca349 tr. Ca326 xxxxx	Ca349 xxx Ca236 x Co ₃ O ₄ tr.
	3 : 4		Ca349 xxxxx Ca326 x	Ca349 xxxxxx Ca326 tr.	Ca349 xxx Ca326 x	

Number of "x" is proportional to the most intense peak of the relevant phase